Concentration Predictions of Eutectic LiCl-KCl Mixtures Containing Multiple Lanthanides

Devin Rappleye, Michael Simpson

Department of Metallurgical Engineering
University of Utah
135 S 1460 E Rm 412, Salt Lake City, UT 84112

Sang-Mun Jeong

Department of Chemical Engineering
Chungbuk National University
Cheongju, Chungbuk 361-763, Republic of Korea

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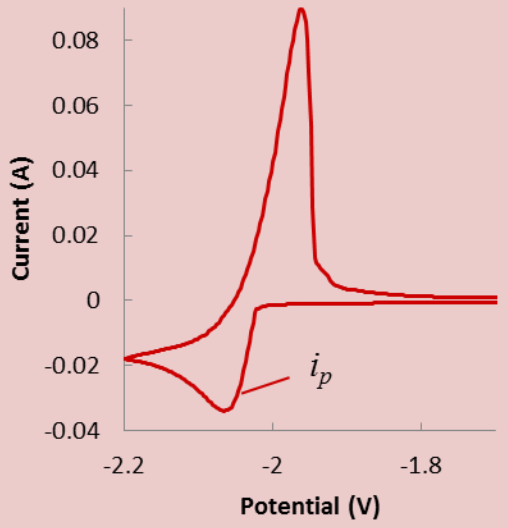
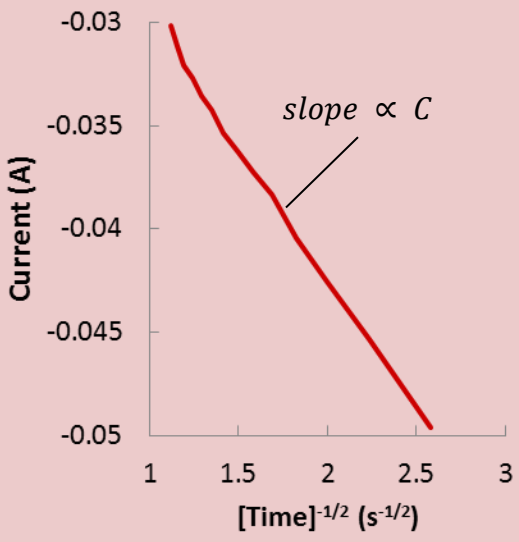
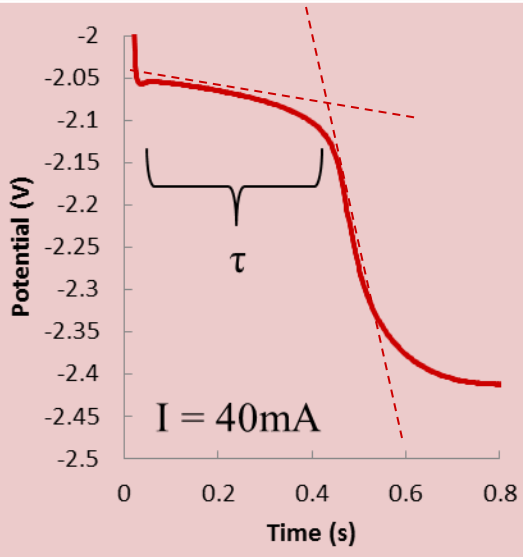
Online Monitoring

Electrochemical Methods

Cyclic Voltammetry	Chronoamperometry	Chronopotentiometry
$i_p = 0.4463A\sqrt{\frac{(nF)^3 D\nu}{RT}}C$	$i(t) = nFA\sqrt{\frac{D}{\pi t}}C$	$i(\tau) = \frac{nFA}{2}\sqrt{\frac{D\pi}{\tau}}C$

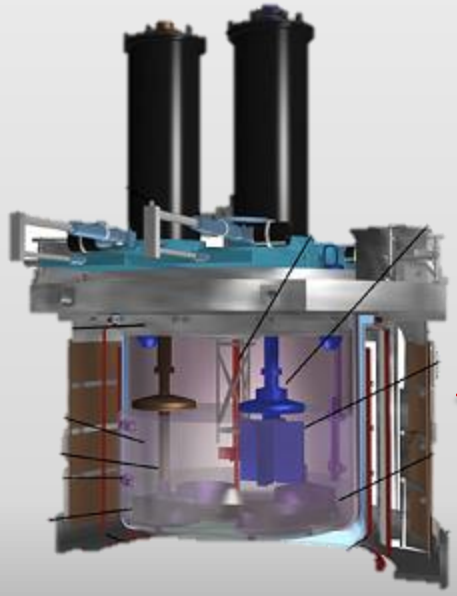






Interference

- Multiple Analytes

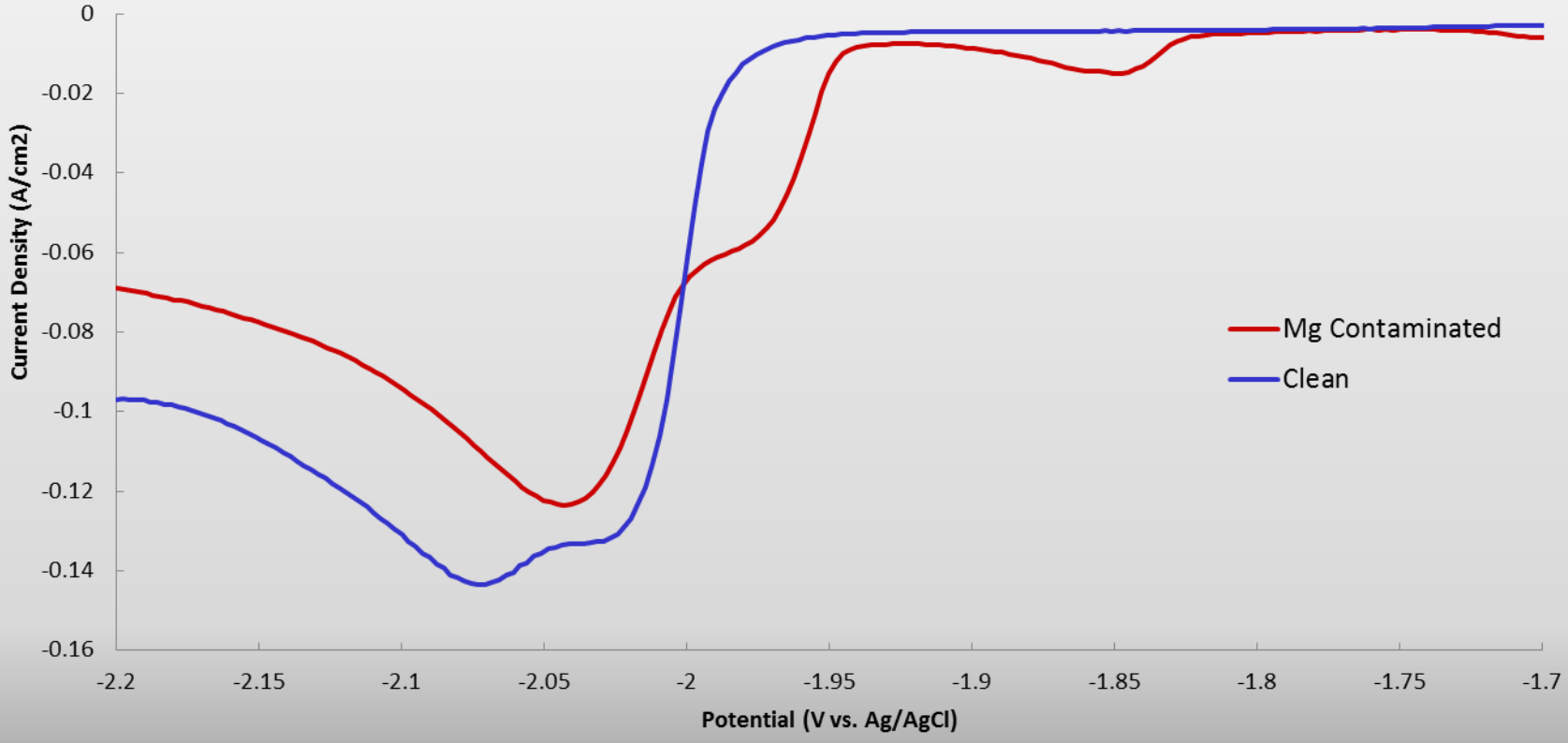


*Taken from: http://seniordesign.engr.uidaho.edu/2010-2011/inl/Images/Hot%20Cell/MarkIVElectrorefiner.png

Redox Couple	$E^{o'}$ (vs. Cl_2/Cl^-)
Zr^{2+}/Zr	-1.98
U^{3+}/U	-2.52
Np^{3+}/Np	-2.67
Pu^{3+}/Pu	-2.75
Cm^{3+}/Cm	-2.86
Am^{2+}/Am	-2.88
Gd^{3+}/Gd	-2.95
La^{3+}/La	-3.11

*Values from Zhang, J. Nucl. Mater. Vol. 447, pp. 271-284

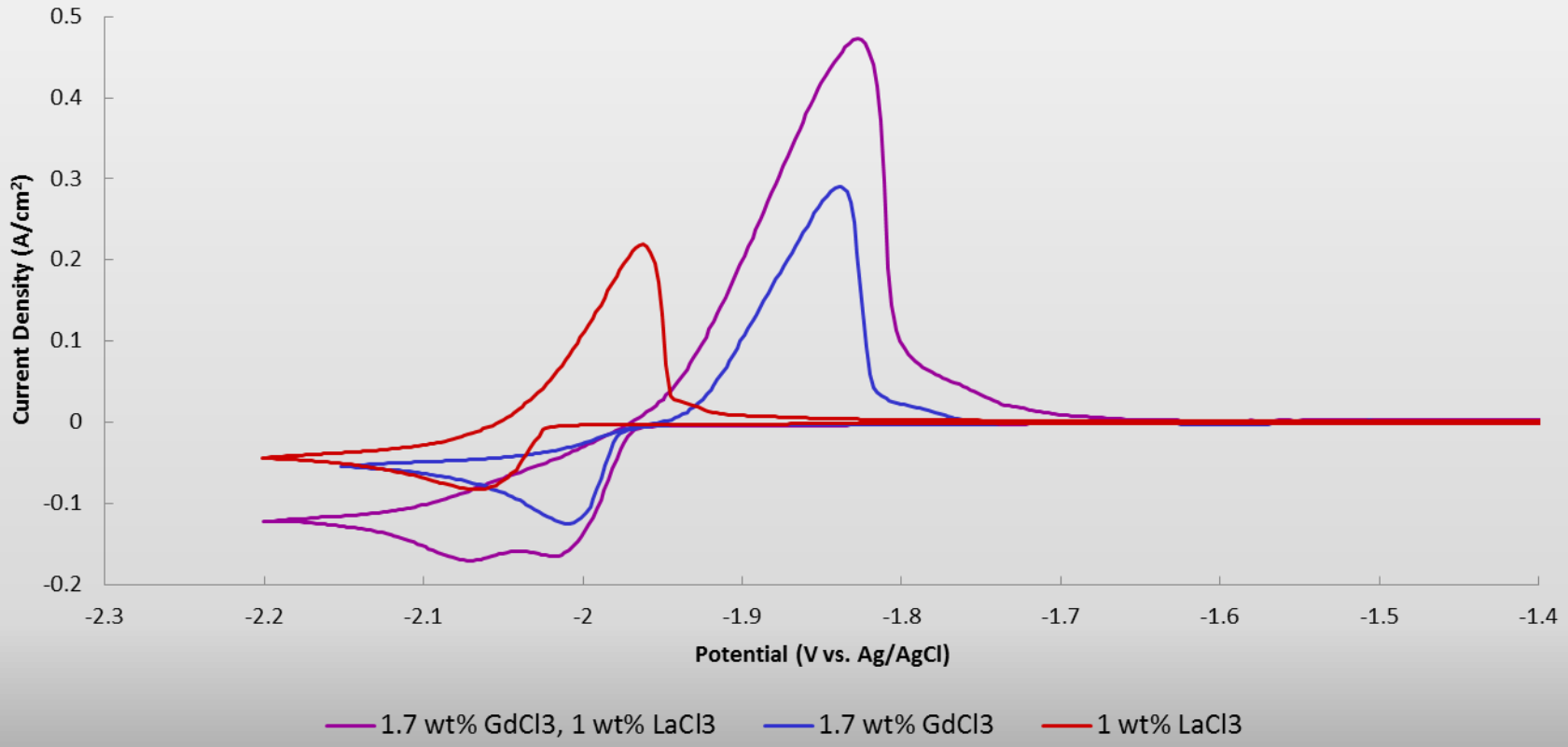
Interference



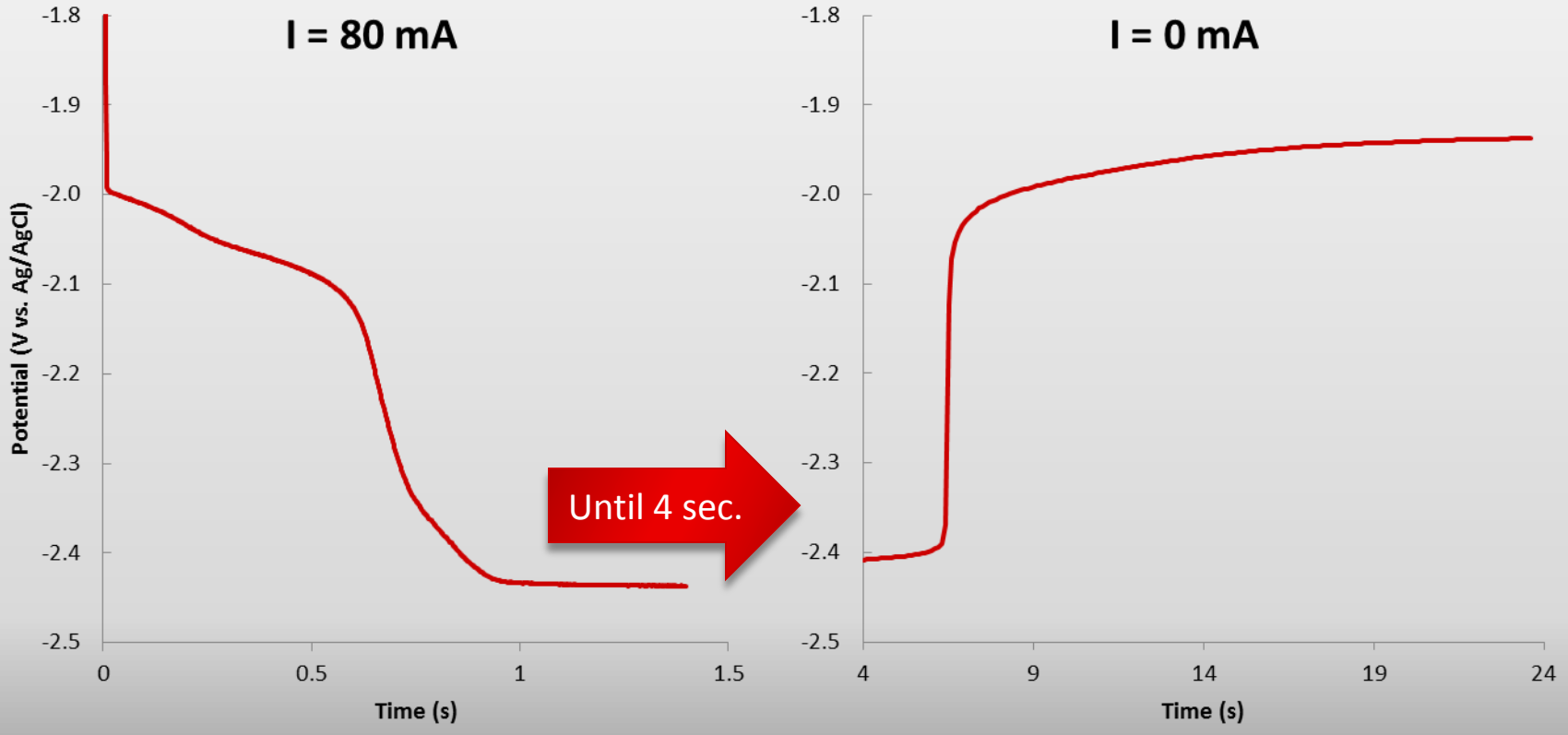
Nuclear Pyrometallurgy Laboratory

- Inert Ar Glovebox
  - O_2 < 1 ppm
  - H_2O < 1 ppm
- T = 773 K
- Alumina Crucible
- WE – 1mm Mo wire
- CE – Gd Rod [6.35 mm x 25 mm]
- RE – 1 wt% AgCl in Pyrex tube
- Chemicals:
  - $GdCl_3$, $LaCl_3$, Eutectic LiCl-KCl
  - 99.99% Ultra Dry

$GdCl_3$ & $LaCl_3$ Cyclic Voltammetry



$GdCl_3$ & $LaCl_3$ Chronopotentiometry



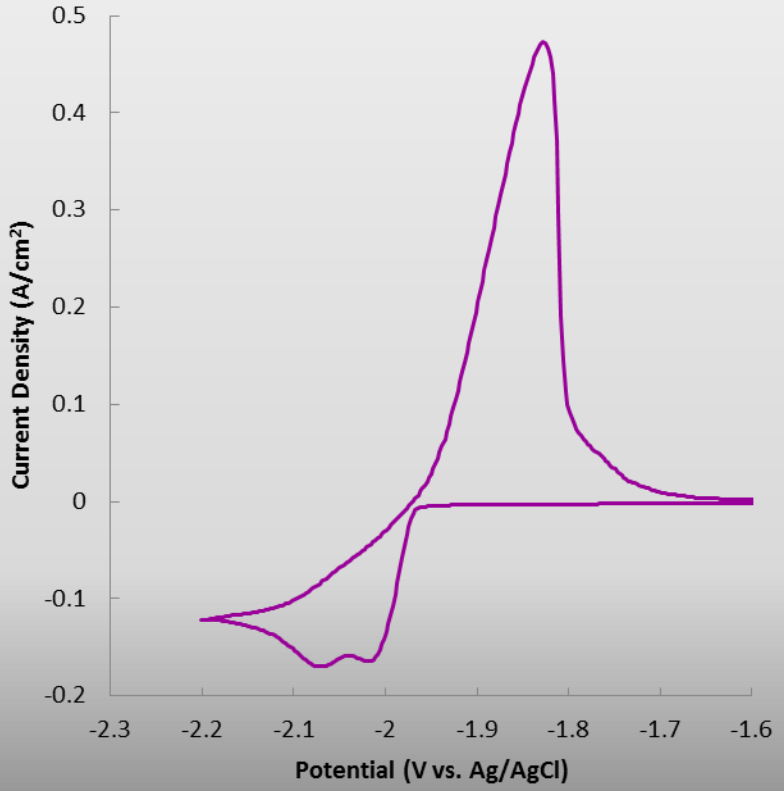
$GdCl_3$ & $LaCl_3$ Electrochemistry

- Deposited/Reduced separately
- Deposited metals form alloy
- Stripped/Oxidized together
- Significant overlap of reduction current
  - Interference for concentration predictions

"If you torture the data long enough, it will confess"
– Ronald Coase

Concentration Prediction Methods

- Cyclic Voltammetry
  - Separate
    - Peak Height Analysis
  - Together
    - Principle Component Regression (PCR)

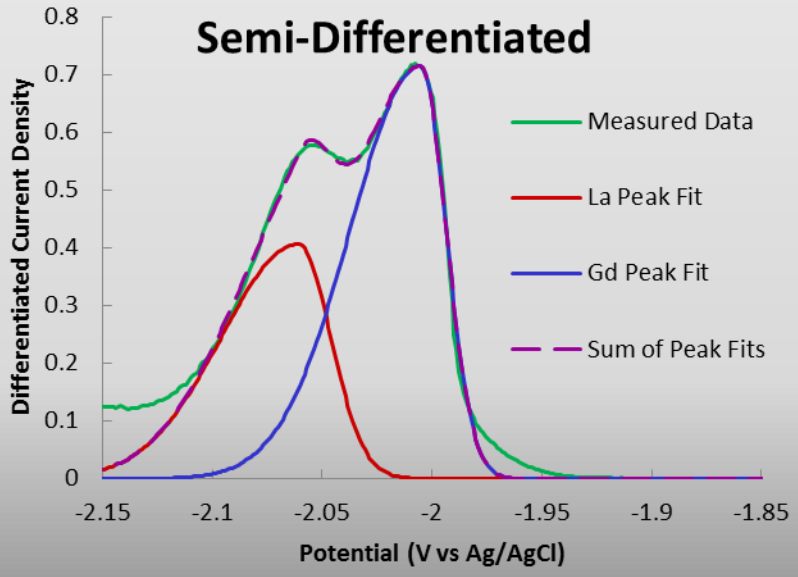


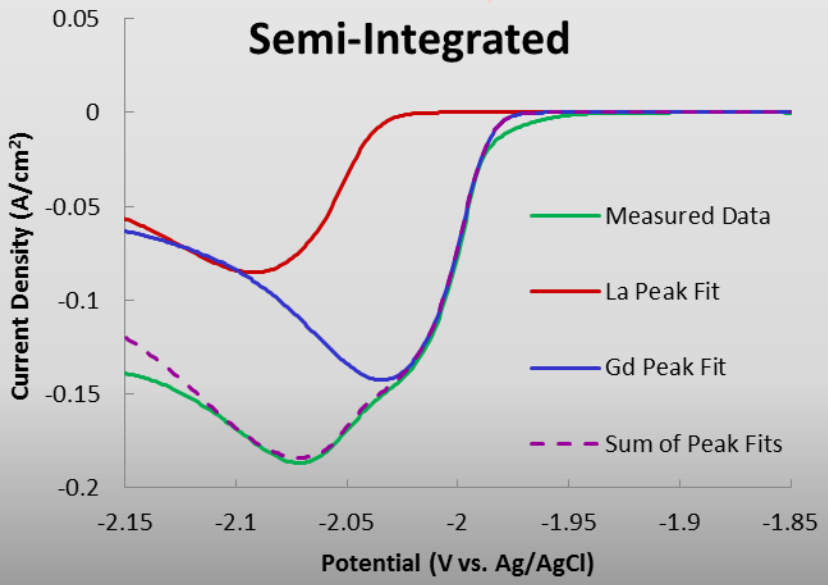
Peak Separation

Semi-Differentiation
- Better Separation
- More Symmetrical

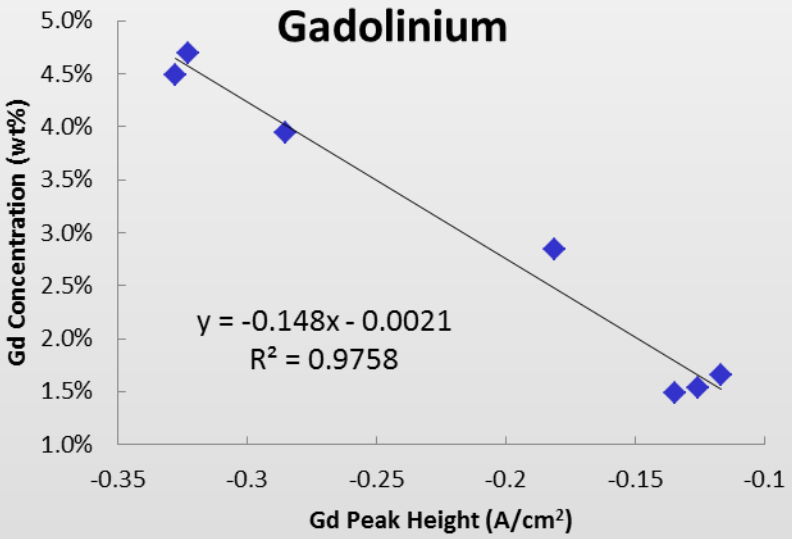
Peak Fit
- Bifurcated Gaussian

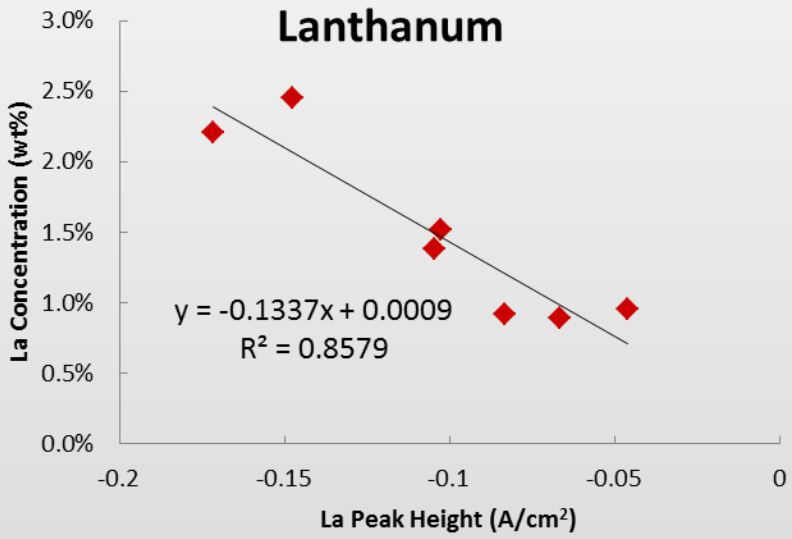
Semi-Integration
- Fitted Peaks





Peak Separation Results



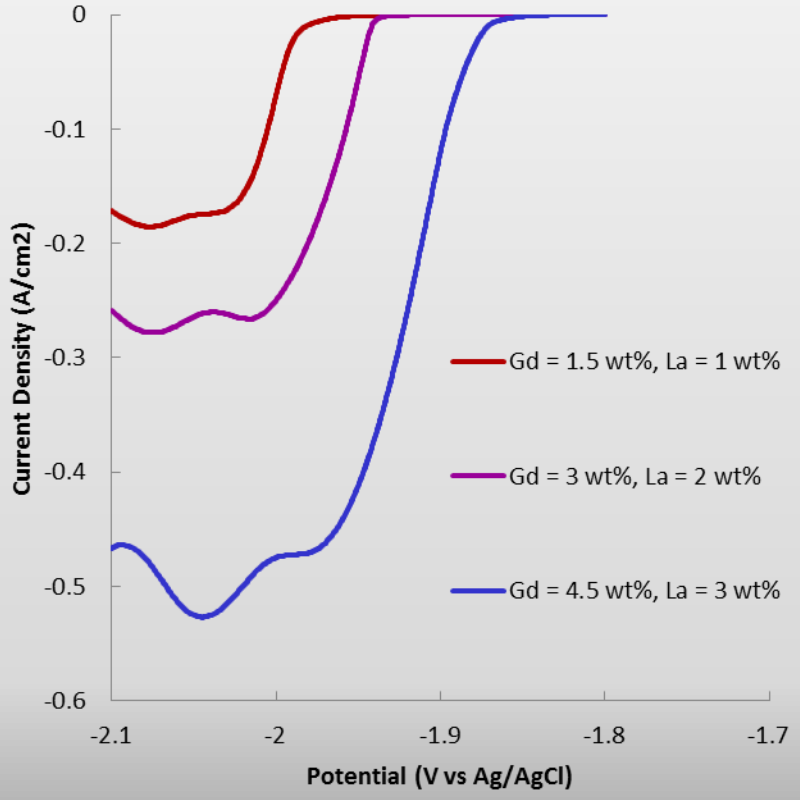


Unknown	#1	#2
Measured (wt%)	1.81	3.64
Predicted (wt%)	2.16	3.63

Unknown	#1	#2
Measured (wt%)	0.97	2.33
Predicted (wt%)	1.02	2.29

Principle Component Regression (PCR)

- Uses all the data
- Identify main contributors to variance from a training set
  - Principal Components (PCs)
- Training Set
  - Gd = 1.5, 3, 4.5 wt%
  - La = 1, 2, 3 wt%
- Regress the PCs with concentration
- Predict unknown composition

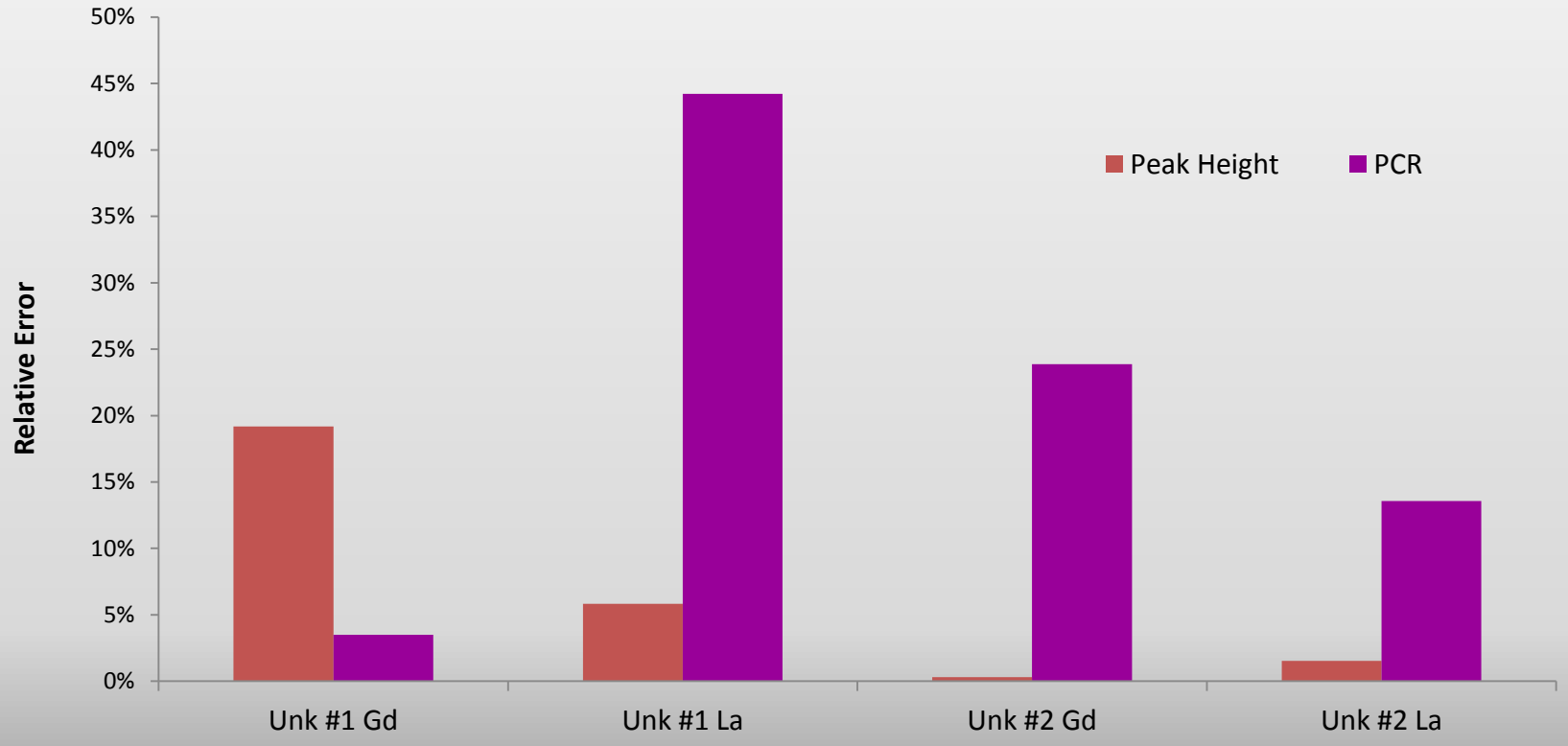


PCR Results

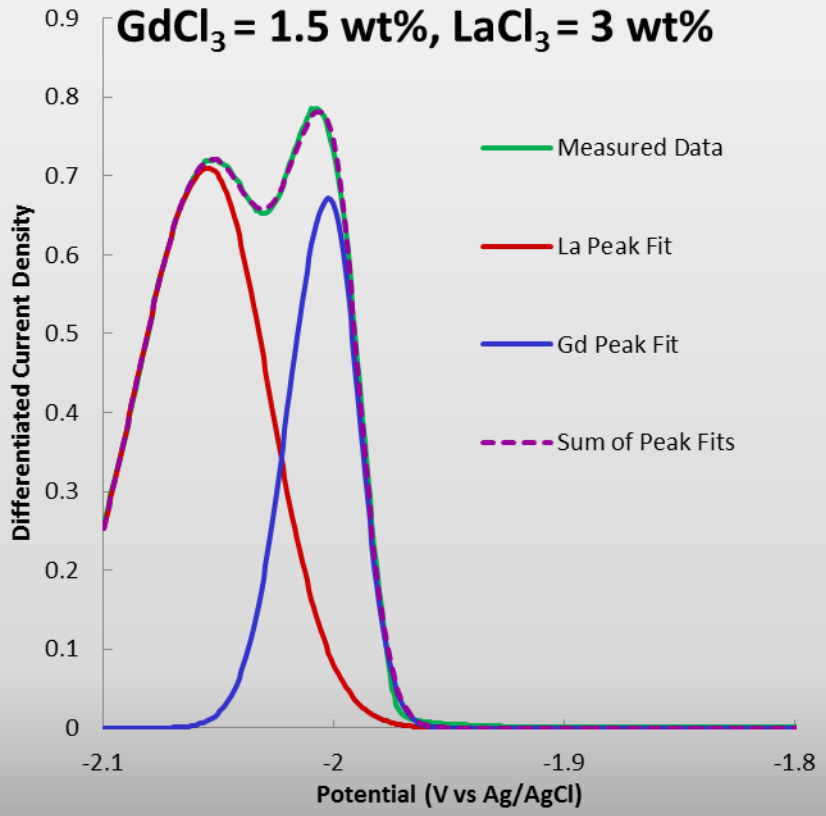
- Mixed Results:
  - Unknown #1
    - Good Gd agreement
    - Bad La agreement
  - Unknown #2
    - Bad Gd agreement
    - Good La agreement

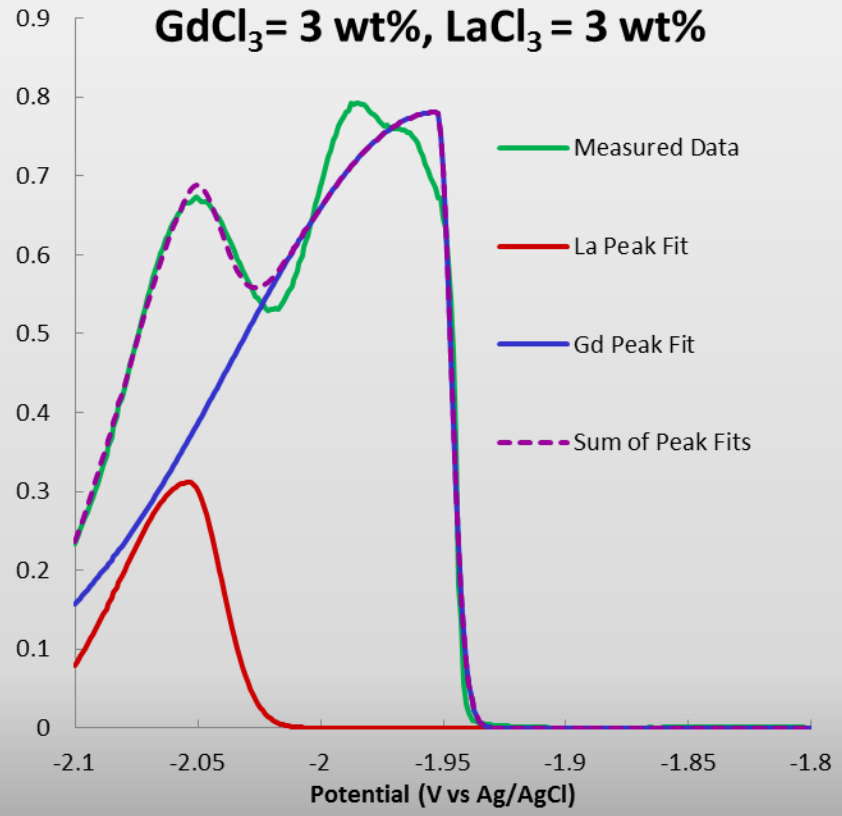
Unknown		$GdCl_3$ (wt%)	$LaCl_3$ (wt%)
#1	Measured	1.68	0.99
	Predicted	1.67	1.60
#2	Measured	3.73	2.49
	Predicted	4.63	2.62

Peak Height vs. PCR



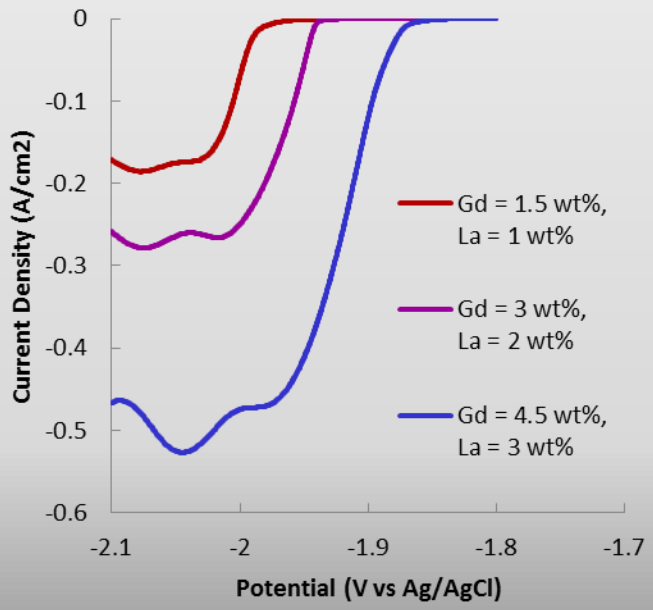
Peak Fitting Challenges





PCR Challenges

- Reducing variations unrelated to concentration:
  - Working electrode surface
  - Reference electrode shift
  - Deposit growth
- Possible solutions:
  - Add analyte to melt
  - Increase scan rate



Moving Forward

- Generate more uniform data
  - Vary concentrations within same experiment
- Develop better peak fitting criteria
- Other methods:
  - Model Fit
    - ERAD
  - Multiple Electrochemical Methods
    - CV + CA
- Additional multicomponent systems
  - Less interaction
  - Further spaced

"Even if you're on the right track, you'll get run over if you just sit there"
– Will Rogers